## (19) World Intellectual Property Organization International Bureau



## 

## (43) International Publication Date 28 June 2001 (28.06.2001)

#### PCT

## (10) International Publication Number WO 01/46490 A1

(51) International Patent Classification<sup>7</sup>: C23C 16/44, H01J 37/32

94583 (US). OUTKA, Duane [US/US]; 15 Gazania Terrace, Fremont, CA 94536 (US).

- (21) International Application Number: PCT/US00/32441
- (22) International Filing Date: 8 December 2000 (08.12.2000)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 09/469,286

22 December 1999 (22.12.1999) U

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:

US

09/469,286 (CON)

Filed on

22 December 1999 (22.12.1999)

- (71) Applicant (for all designated States except US): LAM RESEARCH CORPORATION [US/US]; 4650 Cushing Parkway, Fremont, CA 94538 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): RICHARDSON, Brett, C. [US/US]; 3709 Tortosa Ct., San Ramon, CA

Terrace, Fremont, CA 94536 (US).

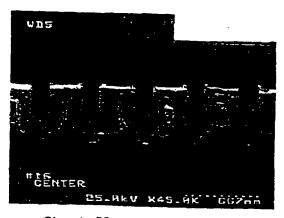
- (74) Agent: PETERSON, James W.; Burns, Doane, Swecker & Mathis, LLP, P.O. Box 1404, Alexandria, VA 22313-1404 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

#### Published:

With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## (54) Title: METHOD OF CLEANING AND CONDITIONING PLASMA REACTION CHAMBER



Step 1=30 sec., Step 2=15 sec. 15 BC13/45 C12, (ROx=7154 A) (57) Abstract: A method for cleaning and conditioning interior surfaces of a plasma chamber in which substrates such as silicon wafers are processed. The method includes cleaning the chamber such as by a wet clean or in-situ plasma clean, introducing a conditioning gas into the chamber, energizing the conditioning gas into a plasma state, depositing a polymer coating on the interior surfaces and processing a substrate. The conditioning step can be preformed without a substrate such as a wafer in the chamber and the processing step can be carried out without running conditioning wafers through the chamber prior to processing production wafers. In the case of plasma chamber used for etching aluminum, the conditioning gas can include a fluorine-containing gas, a carbon-containing gas and a chlorine-containing gas.

WO 01/46490 A1

BEST AVAILABLE COBY

WO 01/46490 PCT/US00/32441

-1-

# METHOD OF CLEANING AND CONDITIONING PLASMA REACTION CHAMBER

#### **Background of the Invention**

5

10

15

20

25

During processing of semiconductor wafers it is conventional to carry out periodic in-situ cleaning of plasma etch and CVD reactors. U.S. Patent No. 5,129,958 discloses a method for cleaning a CVD deposition chamber in a semiconductor wafer processing apparatus wherein fluorine residues in the chamber, left from a prior fluorine plasma cleaning step, are contacted with one or more reducing gases such as silane (SiH<sub>4</sub>), ammonia, hydrogen, phosphine (PH<sub>3</sub>), diborine (B<sub>2</sub>H<sub>6</sub>), and arsine (AsH<sub>3</sub>). Another technique for cleaning and conditioning interior surfaces of plasma CVD reactors is disclosed in commonly owned U.S. Patent No. 5,647,953, the subject matter of which is hereby incorporated by reference. In the past these cleans were done with a wafer in the chamber to cover the electrode, but it has become more common to do waferless cleans.

Other techniques for cleaning plasma reaction chambers are disclosed in commonly owned U.S. Patent No. 5,356,478; in U.S. Patent Nos. 4,657,616; 4,786,352; 4,816,113; 4,842,683, 4,857,139; 5,006,192; 5,129,958; 5,158,644 and 5,207,836 and Japanese Laid-Open Patent Publication Nos. 57-201016; 61-250185, 62-214175, 63-267430 and 3-62520. For instance, in order to remove  $SiO_x$  deposits, a fluorine-containing gas energized into a plasma has been used to clean interior surfaces of the chamber. Fluorine residues remaining after the reactor cleaning can be removed by passing a reducing gas such as hydrogen ( $H_2$ ), silane ( $SiH_4$ ), ammonia ( $NH_4$ ), phosphine ( $PH_3$ ), biborine ( $PH_3$ ) or arsine ( $PH_3$ ) through the reactor.

10

20

25

Chamber conditioning processes are also commonly used where a wafer is placed in the chamber to protect the electrode during conditioning. These conditioning processes are very common for deposition reactors following plasma cleans, and are also common for etch reactors following wet cleans. Sometimes the wafer has a deposited film on it which aids in the conditioning process. As an example, resist coated wafers have commonly been used to accelerate conditioning. Such conditioning steps may use process conditions without bottom electrode power to season the chamber walls.

A problem with using conditioning wafers to season the plasma chamber to obtain reproducible process conditions when processing production wafers is that such conditioning wafers add cost and cause slowdown in production.

Accordingly, it would be desirable for a conditioning treatment which is more economical in terms of cost and production efficiency.

#### **Brief Description of the Drawings**

FIG. 1 shows 703 nm emission data during a waferless autoclean process in accordance with the invention:

FIG. 2 depicts a pre-etch structure of 0.25  $\mu$ m profile test wafers;

FIG. 3 is a comparison of profile wafer endpoint traces following chamber conditioning with resist wafers and following the waferless autoclean process in accordance with the invention;

FIGS. 4a-d are photomicrographs of etched structures after waferless autoclean process and waferless recovery steps in accordance with the invention and FIG. 4e is a photomicrograph of an etched structure processed in a chamber conditioned with resist wafers;

FIGS. 5a-d are photomicrographs of etched structures after waferless autoclean process and waferless recovery steps in accordance with the invention

WO 01/46490 PCT/US00/32441

-3-

and FIG. 5e is a photomicrograph of an etched structure processed in a chamber conditioned with resist wafers; and

FIGS. 6a-c are photomicrographs of etched structures after waferless autoclean process and waferless recovery steps in accordance with the invention and FIGS. 6d-f are photomicrographs of etched structures processed in a chamber conditioned with resist wafers.

5

10

15

20

25

#### **Summary of the Invention**

This invention provides a method of cleaning and conditioning a plasma reaction chamber in which substrates are processed, comprising the steps of cleaning the plasma reaction chamber so as to remove deposits built up on surfaces within the chamber, introducing a conditioning gas comprising a fluorine-containing gas and a carbon-containing gas into the chamber, energizing the conditioning gas into a plasma state, depositing a polymer coating on interior surfaces of the chamber, and processing a substrate in the chamber after the depositing step. The term "polymer" coating is intended to describe organic films which may contain etch or deposition by-products.

According to a preferred embodiment of the invention, the energizing step is carried out by exposing the conditioning gas to an inductive field generated by resonating a radio frequency current in an RF antenna coil, the RF antenna coil being disposed external to the chamber, proximate to a dielectric shield which forms a part of an enclosure of the chamber. Further, the cleaning step can be carried out by opening the chamber and performing a wet clean or the cleaning step can be carried out by introducing a cleaning gas into the chamber, energizing the cleaning gas into a plasma state, and contacting the interior surfaces with the plasma to remove the deposits. In the preferred method, the conditioning step is carried out while the chamber does not contain a substrate therein and/or the substrate comprises a production wafer and the processing step is carried out without processing conditioning wafers in the chamber prior to processing the

10

15

20

25

production wafer. Also, the conditioning step can be carried out without applying power to an RF biasing electrode of a substrate support on which the substrate is supported during the processing step.

In cleaning an aluminum etch reactor, the conditioning gas can further comprise a chlorine-containing gas so that the polymer deposited in the depositing step will include chlorine therein and the processing step comprises etching an aluminum layer on the production wafer. In such a case, the conditioning gas can include  $Cl_2$ ,  $BCl_3$ ,  $CCl_4$ ,  $SiCl_4$  or mixture thereof. For example, the conditioning step can be carried out in one or more steps using  $CHF_3$ ,  $BCl_3$  and/or  $Cl_2$  as the conditioning gas. The chamber pressure during the conditioning step can be in the range of from about 5 to 80 mTorr and/or a plasma generating antenna can be supplied 200 to 1000 Watts during the conditioning step.

## **Detailed Description of the Preferred Embodiments**

This invention provides an economical method of cleaning and conditioning a plasma reaction chamber in which substrates are processed. The method includes cleaning the plasma reaction chamber so as to remove deposits built up on surfaces within the chamber, introducing a conditioning gas comprising a fluorine-containing gas and a carbon-containing gas into the chamber, energizing the conditioning gas into a plasma, depositing a polymer coating formed by the plasma on interior surfaces of the chamber, and processing a substrate in the chamber after the depositing step.

In a preferred embodiment, the invention provides a waferless plasma clean recovery process for conditioning chambers used for plasma etching an aluminum film stack. The process for plasma etching of Al produces a by-product which deposits throughout the reactor. Eventually this by-product reaches a thickness where it no longer sticks to the reactor wall and particles are shed which

WO 01/46490 PCT/US00/32441

-5-

contaminate the substrate being etched. When this happens, the reactor must be opened and cleaned with a wet clean process.

5

10

15

20

25

The process of preparing a reactor for cleaning, along with the actual clean process and the steps required to condition the chamber following an open chamber clean can require a substantial amount of time. To maximize productivity in a wafer fab, it is desirable to extend the time between opening the chamber to do such open chamber cleans. One method for doing this has been to run plasma cleans, which are capable of reducing the etch by-product deposited in the chamber resulting in a extended time between open chamber cleans. However, since plasma cleans alter the chamber condition by removing the reactor deposits, there is typically a process shift following the plasma clean. As a result, the aluminum etch rate, etch profiles and feature CDs (critical dimension) can shift outside of the acceptable range for the device being manufactured. If a plasma clean is used, wafers are cycled through the chamber to recondition the walls prior to etching product wafers.

In processes wherein a wafer is needed in the chamber for conditioning, a special wafer type may also be needed. This limits the applicability of plasma clean processes for Al etching in a production environment because it would be disruptive to production flows to have to load special wafers into the chamber and run a conditioning process after a plasma clean. As a result, in production, plasma cleans would not be used and the reactors would need to be opened more frequently for long wet clean procedures. Thus, the reactor availability advantage of using plasma cleans to extend the wet clean time is negated by the burden of reconditioning the chamber with a special wafer type.

The invention provides a process that can be run without a wafer in the chamber to recondition the chamber following a plasma clean. The by-product deposition from Al etching has been shown to contain a large amount of organic material. The deposition is present throughout the etch process and participates in

10

15

20

the process by providing a source of sidewall passivation, as well as recombination and adsorption sites for reactant species. The deposition can be cleaned by a plasma containing  $O_2$ . However this leaves some residual  $O_2$  in the chamber. Further, the addition of  $O_2$  to Al etching gases is known to increase the Al etch rates and can have an effect on etch profile results.

To recondition the chamber following a plasma clean, it is desirable to remove or bind the residual O<sub>2</sub> so that the etch process is not affected. It is also desirable to provide organic deposits that participate in the process the same way that by-product deposition does. In a waferless conditioning process, this must be done without attack of the wafer chuck which is not covered or protected during the process.

The preferred method for doing this is to run a plasma processing using BCl<sub>3</sub> and CHF<sub>3</sub>. In an inductively coupled plasma etcher such as the TCP 9600<sup>TM</sup> etcher available from LAM Research Corporation, the process is run by applying high RF power to the top electrode (TCP<sup>TM</sup> power) source but without power applied to the bottom electrode which provides an RF substrate bias during wafer processing. This results in low plasma potential and prevents attack of the wafer chuck. BCl<sub>3</sub> is capable of scavenging residual O<sub>2</sub> from the chamber while CHF<sub>3</sub> is a source of deposition of organic materials on the chamber walls. BCl<sub>3</sub> is also a source of C1 which is present in the etch by-product deposition. Typical process conditions and ranges for a TCP 9600<sup>TM</sup> etch reactor are shown in Table 1.

		Tat	ole 1		
	Process Con	ditions for the	Waferless Rec	overy Proces	s
	Pressure	TCP™ Power	Bias Power	BCl <sub>3</sub>	CHF <sub>3</sub>
Typical	50 mt	700 watts	0 watts	15 sccm	37 sccm
Range	10-99	400-1200	0-5	10-30	10-60

Depending on the Al etch stack and process requirements, a second step of the waferless recovery process may be required. If the Al etch process ends with a step that does not contain CHF<sub>3</sub>, a final step of the recovery process that eliminates CHF<sub>3</sub> will improve process recovery. An example of a 2 step waferless recovery process is shown in Table 2.

<del></del>		- :	Table 2			
		Two Step W	aferless Reco	very Proces	s	
	Pressure	TCP™ Power	Bias Power	BCl <sub>3</sub>	C1 <sub>2</sub>	CHF <sub>3</sub>
Step 1	50 mt	700 watts	0 watts	15 sccm		37 sccm
Step 2	15 mt	450 watts	0 watts	30 sccm	30 sccm	

10

5

While BCl<sub>3</sub> was selected for it's O<sub>2</sub> scavenging capability, other gases such as CCl<sub>4</sub> and SiCl<sub>4</sub> would be suitable alternatives. The chlorine concentration could be raised by adding Cl<sub>2</sub> Likewise, many chlorocarbon, fluorocarbon and CFC gases could easily be substituted for CHF<sub>3</sub> as a polymer source. Diluent gases such as He and Ar could be added while maintaining an effective process.

15

The waferless recovery process can be run without special wafer types, eliminating the need for operator intervention. An additional benefit to not needing wafers for the recovery process is that there is minimal loss to production time as there is no overhead time used to load a wafer into the chamber for the clean or conditioning step. The direct result of this is a higher availability of the reactor for etching valuable product.

20

25

Use of the waferless recovery step following a reactor wet clean has the advantage of reducing wet clean recovery time as well. For instance, compared to a conditioning process wherein it takes around 90 minutes to run 50 resist wafers through the wet-cleaned chamber, according to the invention the conditioning process can be completed in around 5 minutes or less. Thus, the conditioning

10

15

process according to the invention can cut the recovery time following a chamber clean by over 50%, and even 80% or higher. Further, the chamber can be conditioned in less time without using or minimizing use of conditioning wafers. Increased availability of the reactor for product, and reduced non-production wafer requirements are both advantageous for increased customer profitability.

## Test Data and Results, TCP™ 9600SE™ SystemSystem Baseline

This study was started with a baseline of the 9600 SE<sup>TM</sup> system. The chamber was wet cleaned, and blanket photoresist (PR) wafers were run to condition the chamber. Aluminum etch rate wafers were run on the conditioned chamber to establish the etch rate target for the waferless recovery process development work. The process etch rate shift due to execution of a long O<sub>2</sub> waferless autoclean (WAC) was established. Etch rate results from the baseline tests are shown in Table 3.

	Ta	ble 3				
Aluminum	Etch Rate Baseline Data	Before and After an	8 min. O <sub>2</sub> WAC			
Wafer ID	Average Step Height	% Change Due to Clean	Pressure Control Valve Angle (% open)			
Pre clean #1	4602		36.8			
Pre clean #2	4659		36.1			
Post WAC	5254	13.5%	35.5			

## 20 Chamber/Process Recovery Considerations

Several mechanisms have been proposed to account for the etch rate increase following the WAC. One proposal for etch rate recovery was to use Cl<sub>2</sub> flow control rather than pressure control valve position to regulate pressure since

10

15

20

25

Al etch rate scales with Cl<sub>2</sub> flow. The interaction of Cl<sub>2</sub> with clean and conditioned chamber walls will be different (adsorption, recombination, etc.), and if this affected the net Cl<sub>2</sub> concentration it is possible that this would be reflected in the chamber pressure for a fixed pressure control valve position.

The addition of small amounts of  $O_2$  to some aluminum etch processes has also been reported to increase Al etch rate. Residual  $O_2$  in the chamber was proposed as a possible cause of etch rate increase after WAC. A conditioning process that scavenges residual  $O_2$  could address this issue.

Cycling resist wafers is a very effective method for chamber conditioning and is the recovery procedure recommended after wet clean. This points to the role of carbon in etch by-product as a significant factor in chamber conditioning. Also, the effectiveness of an O<sub>2</sub> WAC for chamber cleaning indicated that the chamber walls are conditioned with organic deposits. Use of an organic depositing chemistry for chamber conditioning could address this issue.

The proposed mechanisms were considered and a series of experiments were conducted to determine the significant effects.

For the Cl<sub>2</sub> flow control option to work, there must be a measurable difference in the pressure for a fixed pressure control valve position before and after the waferless clean. Alternatively, we would expect to see the pressure control valve open wider to maintain a set pressure after the WAC if Cl<sub>2</sub> flow control could be effective. The pressure control valve position before (2 wafers) and after WAC was measured. The change in position is small and, if significant, in the wrong direction for Cl<sub>2</sub> flow control to be effective for etch rate recovery.

Based on this, the approach investigated for chamber recovery was to look at the feasibility of a waferless recovery step (WRS). With the proposed mechanisms in mind, 3 chemistries were investigated, namely Cl<sub>2</sub>/BCl<sub>3</sub> (O<sub>2</sub> Scavenging), Cl<sub>2</sub>/CHF<sub>3</sub> (organic depositing), BCl<sub>3</sub>/CHF<sub>3</sub> (combined scavenging and depositing).

Scavenging), C1<sub>2</sub>/CHF<sub>3</sub> (organic depositing), BCl<sub>3</sub>/CHF<sub>3</sub> (combined scavenging and depositing).

To test the possible WRS processes, the system was set up to cycle the blanket resist wafer using the baseline Al etch process with the WAC (12 seconds) and WRS process run between each wafer. The 3 WRS steps tested are shown in Table 4. For each test, 30-40 blanket resist wafers were cycled prior to running an Al etch rate test. Table 5 shows the etch rate results. For a conditioned chamber, the Al etch depth is about 4630 A. The BCl<sub>3</sub>/CHF<sub>3</sub> process shows that it is possible to recover the desired Al etch rate following the WAC using a WRS. Assuming etch rate to be a primary indicator of process shift, the feasibility of using a WRS to recover the desired process stability following WAC looks very good.

Table 4 **WRS Process Conditions Tested Parameter** C12/CHF, Cl<sub>2</sub>/BCl<sub>3</sub> BCl<sub>3</sub>/CHF<sub>3</sub> Pressure 20 mt 20 mt 50 mt **ТСРтм** 700 W 700 W 700 W Cl<sub>2</sub> 162 sccm 30 sccm BCI, 54 sccm 15 sccm CHF<sub>3</sub> 37 sccm 37 sccm Step Time 8 sec 15 sec 20 sec

15

5

10

20

10

15

20

25

	Т	able 5
	Etch Depth Results for	or the WRS Process Tests
WRS Process	Al Etch Depth	Change From Conditioned Chamber
Cl <sub>2</sub> /BCl <sub>3</sub>	5445 A	17.6%
Cl <sub>2</sub> /CHF <sub>3</sub>	5300 A	14.5%
BCl <sub>3</sub> /CHF <sub>3</sub>	4671 A	0.9%

### Waferless Clean Frequency

An important part of WAC implementation will be selecting a WAC frequency that minimizes throughput impact while maximizing effectiveness at maintaining a clean chamber. The optical emission at 703 nm was determined to be a suitable WAC endpoint indicator. The signal degrades throughout the WAC process and flattens when the chamber has been adequately cleaned.

A series of tests were run to determine how the required WAC time scales with number of wafers ("N") between WACs. The chamber was cleaned with an extended O<sub>2</sub> plasma to reach a baseline condition. This was followed by a test where the number of wafers between running the WAC was varied and the 703 nm emission was monitored during the WAC step to determine the time required to clean the chamber. Figure 1 shows the endpoint traces from this test. The endpoint signal increases rapidly when RF comes on. As "N" increases, the length of time it takes for the endpoint signal to degrade to the baseline increases, showing the clean time is a function of "N".

Table 6 shows the endpoint time for the WAC vs. "N" as well as the clean time for wafer. Times are shown for the endpoint signal to degrade to baseline as well as degrading to 100 counts above baseline. For these process conditions the unit clean time diminishes as "N" increases from 1-5, however at "N" = 10, the unit cleaning time is increasing. This suggests that an optimal clean frequency might be somewhere between 5-20 wafers.

		Table (	5		
WAC Endpo	oint and Unit	Clean Time	(seconds) vs.	WAC Frequ	иепсу
WAC Time	10 wafers	5 wafers	3 wafers	1 wafer	1 wafer
Full WAC	265	71	56	37	38
Emission 1=100	143	45	40	23	24
		Unit Clean	Time		
Full WAC	26.5	14.2	18.66667	37	38
Emission 1 = 100	14.3	11.4	13.33333	23	24

## WRS Etch Rate Recovery

10

15

20

5

The BCl₃/CHF₃ WRS was tested on the 9600PTX™ system using the process conditions for the Al etch, WAC, and WRS steps shown in Table 7. The system was initially conditioned by cycling 57 blanket resist wafers with the Al etch process conditions. The Al etch rate for the conditioned chamber was measured. Following this the chamber was over cleaned using the WAC process conditions with a 7 minute clean time. The 703 nm endpoint signal was used to verify the clean time was sufficient. Next, 29 additional blanket resist wafers were cycled through the system using the Al etch process, but the WAC and WRS steps were used between each wafer. The Al etch rate was then checked again following a WAC and WRS step. The etch depth results are shown in Table 8. The etch rate following the WAC and WRS was not significantly different than the etch rate of the seasoned chamber (1.6% lower).

· · · · · · · · · · · · · · · · · · ·				Table '	7			
		Al Etch,	WAC,	and WRS	Process (	Conditions		
Process	Pressure	TCP <sup>TM</sup> (W)	Bias (W)	Flows (sccm)			He Cooling	Time (S)
Cycle	12 mt	350	78	74 Cl <sub>2</sub>	30 BCI <sub>3</sub>	5 CHF <sub>3</sub>	10 T	65
Al Etch Depth	12 mt	350	78	74 Cl <sub>2</sub>	30 BCI,	5 CHF,	10 T	35
WAC	32 mt	700	0	500 O <sub>2</sub>				12
WRS	50 mt	700	0		15 BCl <sub>3</sub>	37 CHF,	<u> </u>	20

20

5

	Table 8			
	th Depth of the Condition Following the WAC+W	•		
Test Condition				
Conditioned Chamber	3835			
Post WAC+WRS	3773	~1.6%		

### 15 Profile Etch Tests

Etch tests were performed to determine the effect of the WAC and WRS on etch profile. FIG. 2 illustrates the profile test wafer structure before etching.

A small matrix was run to evaluate the importance of step time and BCl<sub>3</sub>:Cl<sub>2</sub> ratio in the recovery step on etch profile. Table 9 shows the 4 processes run in a ½ factorial matrix. FIG. 3 shows the endpoint trace for a wafer etched following the 2 step recovery process. The endpoint trace closely matches the trace of a wafer etched in a resist conditioned chamber. Further, the etch rates through the BARC, Ti and TiN layers match the etch rates of such layers in the

resist conditioned chamber. All wafers etched following the 2 step recovery had similar traces.

		Table 9		
Baseline Process				
Step 1: 50 mt/70	00 W TCP™/37	sccm CHF <sub>3</sub> /15	sccm BCl <sub>3</sub> /"X"s	seconds
Step 2: 15 mt/45			•	
Matrix	Wafer 16	Wafer 17	Wafer 18	Wafer 19
Step 1 Time ("X")	30 sec	20 sec	20 sec	30 sec
Step 2 Time ("Z")	15 sec	7 sec	15 sec	7 sec
BCl <sub>3</sub> /Cl <sub>2</sub> Flows	15 sccm BCl <sub>3</sub>	15 sccm BCl <sub>3</sub>	30 sccm BCl <sub>3</sub>	20 sccm BCl <sub>3</sub>
("Y")/(60- <b>"</b> Y")	45 sccin Cl <sub>2</sub>	45 sccm Cl,	30 sccm Cl,	30 sccm Cl,

10

15

20

5

FIGS. 4a-e and 5a-e show the etch profiles from wafers etched as part of the WAC and WRS matrix compared to the result of etching in a resist conditioned chamber. The differences in etch profile between the wafers is subtle in most cases showing that the 2 step recovery process has a reasonable process window. Some notable trends from the matrix include:

- A chlorine base second recovery step improves the etch profile recovery.
- Use of a higher %Cl<sub>2</sub> in the second recovery step appears to result in reduced CD growth in the feature top compared to the reference wafer.

The effect is stronger for a short first recovery step time (see wafer 17).

- Use of the longer first recovery step improves process latitude for sidewall smoothness.
- Wafers etched with the shorter second step times more closely matched the remaining oxide on the reference wafer.

FIGS. 6a-f show additional SEMs comparing the result of wafer 19 to the conditioned chamber result. Note in these SEMs the profile of isolated features is

10

15

also reproduced, and the resist profile and sidewall deposition are matched by the 2 step recovery process as well.

It appears that running the first recovery step long enough to generate some organic film in the chamber, followed by running a brief chlorine chemistry is sufficient to recover the process after the WAC. The chlorine chemistry step may not be necessary for processes that rely on heavy organic deposition and high bombardment energies to protect the etch sidewall.

Process recovery for etching aluminum after WAC requires that a proper balance be achieved between organic deposition in the chamber and chlorination of the chamber walls. Process recovery for the CHF<sub>3</sub> additive etch process where the etch profile is more sensitive to chemistry balance has been demonstrated. The WRS matrix shows that a 2 step recovery process can be tuned to balance the organic and chlorinated composition in the chamber to a "conditioned" state following the WAC.

While the invention has been described in detail with reference to specific embodiments thereof, it will be apparent to those skilled in the art that various changes and modifications can be made, and equivalents employed, without departing from the scope of the appended claims.

#### Claims:

5

15

1. A method of cleaning and conditioning a plasma reaction chamber in which substrates are processed, comprising the steps of:

cleaning the plasma reaction chamber so as to remove deposits built up on surfaces within the chamber;

introducing a conditioning gas comprising a fluorine-containing gas and a carbon-containing gas into the chamber;

energizing the conditioning gas into a plasma;

depositing a polymer coating formed by the plasma on interior surfaces of the chamber; and

processing a substrate in the chamber after the depositing step.

- 2. The method of Claim 1, wherein the energizing step is carried out by exposing the conditioning gas to an inductive field generated by resonating a radio frequency current in an RF antenna coil, the RF antenna coil being disposed external to the chamber, proximate to a dielectric shield which forms a part of an enclosure of the chamber.
- 3. The method of Claim 1, wherein the conditioning gas further comprises a chlorine-containing gas and the polymer deposited in the depositing step includes chlorine therein.
- 4. The method of Claim 1, wherein the cleaning step is carried out by opening the chamber and performing a wet clean.
  - 5. The method of Claim 1, wherein the cleaning step is carried out by introducing a cleaning gas into the chamber, energizing the cleaning gas into a

plasma state, and contacting the interior surfaces with the plasma to remove the deposits.

- 6. The method of Claim 1, wherein the conditioning step is carried out while the chamber does not contain a substrate therein.
- 7. The method of Claim 1, wherein the substrate comprises a production wafer and the processing step is carried out without processing conditioning wafers in the chamber prior to processing the production wafer.
  - 8. The method of Claim 7, wherein the processing step comprises etching an aluminum film stack on the production wafer.
- 9. The method of Claim 1, wherein the conditioning step is carried out without applying power to an RF biasing electrode of a substrate support on which the substrate is supported during the processing step.
  - 10. The method of Claim 1, wherein the conditioning gas includes Cl<sub>2</sub>, BCl<sub>3</sub>, CCl<sub>4</sub>, SiCl<sub>4</sub> or mixture thereof.
- 15 11. The method of Claim 1, wherein the conditioning gas includes CHF<sub>3</sub> and BCl<sub>3</sub> and/or Cl<sub>2</sub>.
  - 12. The method of Claim 1, wherein the chamber pressure during the conditioning step is in the range of from about 5 to 80 mTorr.
- 13. The method of Claim 2, wherein the RF antenna is supplied 200 to20 1000 Watts during the conditioning step.

- 14. The method of Claim 5, wherein the plasma cleaning gas converts the deposits on the interior surfaces to gas by-products.
- 15. The method of Claim 1, wherein the chamber is a plasma etch chamber.
- 5 16. The method of Claim 15, further comprising a step of etching aluminum on one or more semiconductor substrates in the chamber prior to the cleaning step, the etching step producing the deposits on the interior surfaces of the chamber.
- 17. The method of Claim 15, wherein the conditioning step is followed by introducing one or more semiconductor substrates into the chamber and etching aluminum on the one or more substrates.
  - 18. The method of Claim 1, wherein the conditioning step is performed until an endpoint determined by optical emission or interferometry is reached.
- 19. The method of Claim 1, wherein the conditioning step is carried out in first and second steps, the conditioning gas further including a chlorine-containing gas in the first step and the conditioning gas being fluorine-free in the second step.
  - 20. The method of Claim 19, wherein the conditioning gas comprises 1-30 sccm BCl<sub>3</sub> and 10-60 sccm CHF<sub>3</sub> in the first step and the conditioning gas comprises 20-60 sccm BCl<sub>3</sub> and 20-60 sccm Cl<sub>2</sub> in the second step.

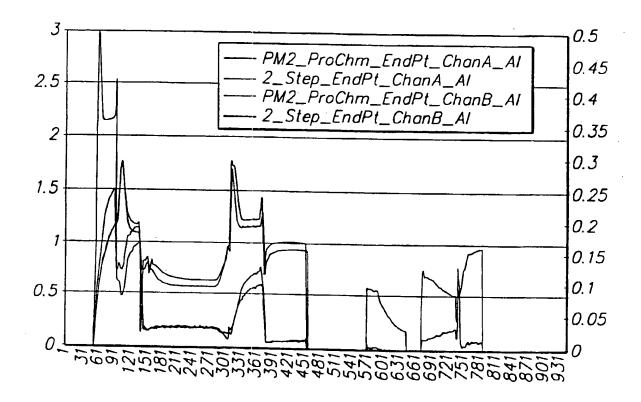


FIG. 3

O 2 Clean, 703 nm Emission

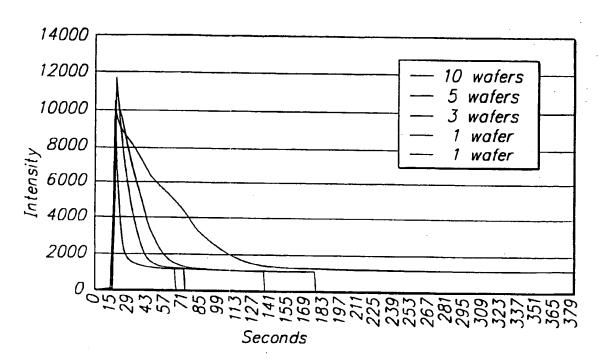


FIG. 1

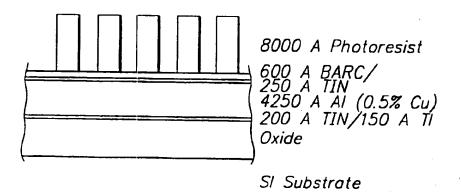
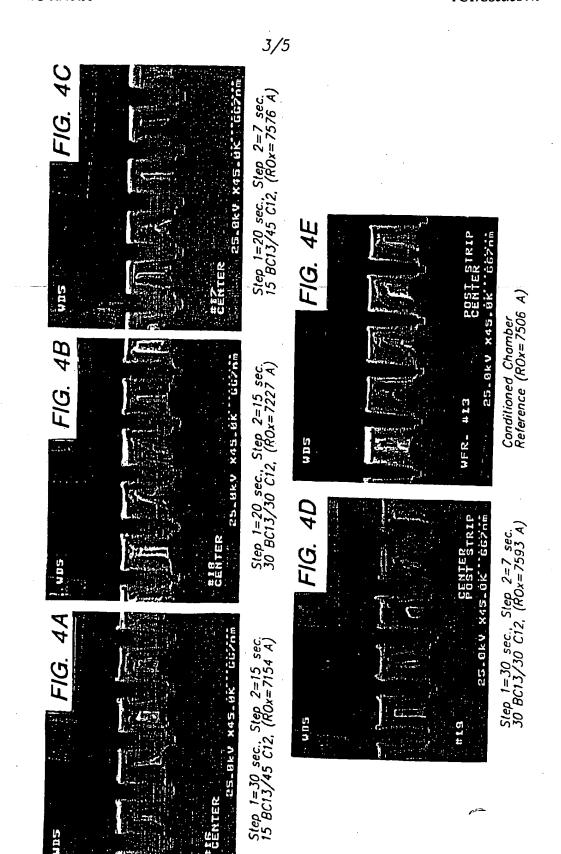
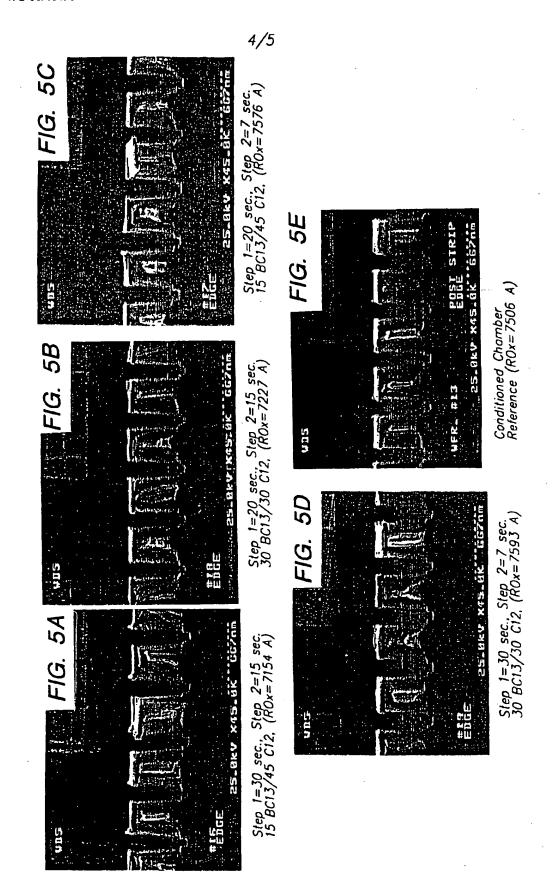


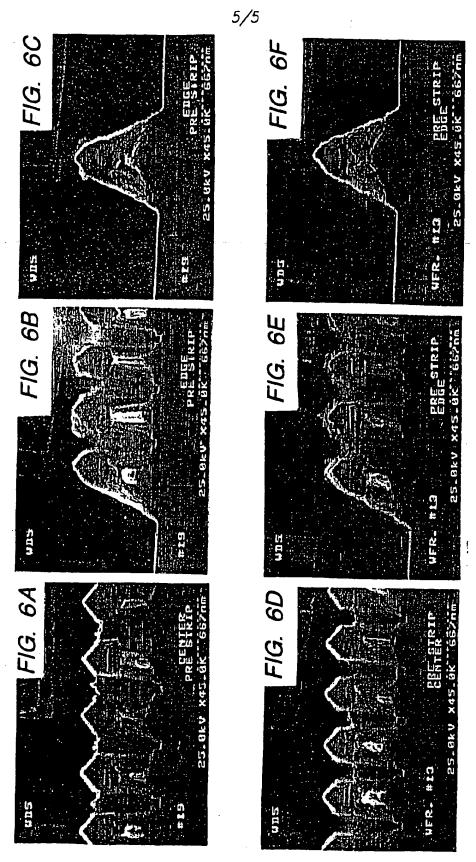
FIG. 2



**SUBSTITUTE SHEET (RULE 26)** 



SUBSTITUTE SHEET (RULE 26)



**SUBSTITUTE SHEET (RULE 26)** 

## INTERNATIONAL SEARCH REPORT

Int tional Application No PCT/US 00/32441

A. CLASSIF	C23C16/44 H01J37/32		
According to	International Patent Classification (IPC) or to both national classification	tion and IPC	·
B. FIELDS			
IPC 7	cumentation searched (classification system followed by classification C23C	n symbous;	
Documental	ion searched other than minimum documentation to the extent that su	uch documents are included in the fields sea	arched
Electronic da	ala base consulted during the international search (name of data bas	e and, where practical, search terms used)	
EPO-In	ternal, PAJ, WPI Data, INSPEC, IBM-T	DB, COMPENDEX	
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the rele	evant passages	Relevant to claim No.
Α	US 5 647 953 A (HARSHBARGER WILLI AL) 15 July 1997 (1997-07-15) cited in the application column 4, line 5 - line 22	AM ET	1-20
A	EP 0 648 858 A (APPLIED MATERIALS 19 April 1995 (1995-04-19) page 3, line 50 -page 4, line 14 page 5, line 9 - line 17 page 6, line 14 - line 50; exampl		1-20
A	US 5 639 341 A (TABARA SUGURU) 17 June 1997 (1997-06-17) column 7, line 7 -column 8, line	6	1-20
Furt	her documents are listed in the continuation of box C.	X Patent family members are listed in	h annex.
• Special ca	ategories of cited documents:	*T* later document published after the inter	mational filing data
consid	ent defining the general state of the art which is not dered to be of particular relevance document but published on or after the international	or priority date and not in conflict with cited to understand the principle or the invention	the application but cory underlying the
"L" docume which		<ul> <li>'X' document of particular relevance; the ci cannot be considered novel or cannot involve an inventive step when the doc 'Y' document of particular relevance; the ci cannot be considered to involve an involv</li></ul>	be considered to current is taken alone takned invention
other	ent referring to an oral disclosure, use, exhibition or means ent published prior to the international filling date but han the priority date claimed	document is combined with one or mo ments, such combination being obvious in the art.  *&* document member of the same patent if	re other such docu- us to a person sidlled
	actual completion of the international search	Date of mailing of the international sea	<del> </del>
9	March 2001	16/03/2001	
Name and	mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk	Authorized officer	
	Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Ekhult, H	

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/US 00/32441

Patent document cited in search repor	t	Publication date		Patent family member(s)	Publication date
US 5647953	Α	15-07-1997	WO	9723663 A	03-07-1997
EP 0648858	Α	19-04-1995	JP	7312363 A	28-11-1995
US 5639341	Α .	17-06-1997	JP JP	2962181 B 8213370 A	12-10-1999 20-08-1996

Form PCT/ISA/210 (patent family armsx) (July 1962)

# This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

| BLACK BORDERS
| IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
| FADED TEXT OR DRAWING
| BLURRED OR ILLEGIBLE TEXT OR DRAWING
| SKEWED/SLANTED IMAGES
| COLOR OR BLACK AND WHITE PHOTOGRAPHS
| GRAY SCALE DOCUMENTS
| LINES OR MARKS ON ORIGINAL DOCUMENT
| REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
| OTHER:

## IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.